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RAW MATERIALS

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ASSESSMENT OF CLAYEY RAW MATERIAL SUITABILITY FOR WALL AND FAÇADE CERAMIC PRODUCTION

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The mineral composition of clayey raw material from 48 deposits in Ukraine with commercial applications is studied. It is determined that the mineral composition of clays affects the properties of ceramic materials based on them. Diagrams in which mineral composition regions for clays with free quartz mass fraction from 30 to 50% which are suitable for the production of wall and façade ceramic obtained at killing temperatures 950 – 1050°C are constructed.

Key words: wall and façade ceramic, polymineral clays, material composition, free quartz, kilning, properties.

In the manufacture of ceramic articles for construction, specifically, wall and façade ceramics, polymineral clays as a basic component of ceramic bodies play a leading role in forming the properties of the materials. This is why studies of the raw materials base for new enterprises devote a great deal of attention to the physical-chemical and ceramic properties of clays on which the qualitative composition and quantitative ratio of clayey materials and the impurities in them have a decisive influence. The mineral composition of clayey raw materials determines the technological properties of the products obtained from them, the phase composition and properties of the ready ceramic materials and ultimately the industrial use of the raw material.

Up to now the industrial use of clayey raw material was determined using diagrams that clearly show the relation between the composition of clays and the types of articles obtainable based on them. Two such diagrams are those of A. I. Avgustinik, which reflect the relation between the chemical composition and the use of the raw material, and A. S. Berkman and I. G. Melnikova's, which show the relation between the particle-size composition and the use of the clays [1, 2]. However, the information that can be obtained using these diagrams is not exhaustive, because the mineral composition of the clays, which directly influences the structure formation processes, the phase composition and the properties of the ceramic material, is not taken into account.

The problem of establishing the dependence of the properties of ceramic materials on the mineral composition of clayey raw material was partially solved by V. F. Pavlov. Such dependences for high-melting clay and fireclays, used in the technology used to produce densely sintered coarse and fine construction ceramic, including ceramic obtained by fast kilning regimes, are analyzed in a monograph by this author [3]. The mineral composition of the overwhelming majority (30 of 38) of the clays studied was represented by combinations of two minerals in which kaolinite predominated. Other authors solved a similar problem for wall ceramic technology using artificial mixtures consisting of double and triple combinations of the main rock-like clayey minerals [4]. In this case pure clayey minerals were studied neglecting impurities, which does not correspond to the real situation usually observed in respect to the material composition of polymineral "brick – crock" clays. As a rule such clayey rocks also contain free quartz, carbonates, feldspars and other materials. The lack of information on the relation between the material composition of polymineral clays and the properties of ceramics obtained on their basis attests to the urgency of research in this direction.

The problem of the present work was to determine the effect of the material composition of polymineral clays on the properties of ceramic materials in order to assess the suitability of raw material of this type for manufacturing different types of coarse building ceramic.

For this, we analyzed the experimentally determined chemical and mineral composition of the clays currently

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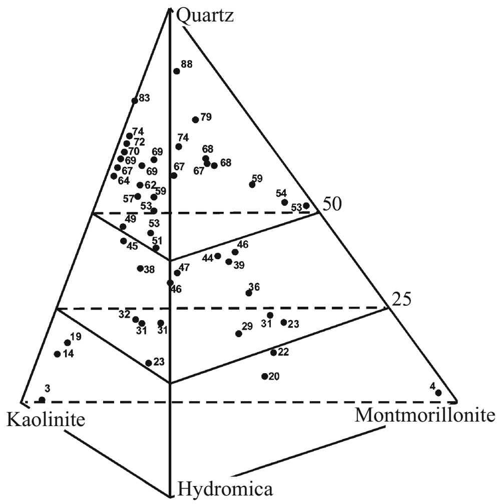

Fig. 1. The mineral composition of the clays used in the manufacture of wall and façade ceramic materials. The numbers represent the quartz content by weight.

used as base raw materials and process additives in the manufacture of wall and façade ceramics. The experimental sample consisted of 48 clays from different deposits in Ukraine. Information on clay composition was obtained from the Khimiya database developed in the Department of the Technology of Ceramics, Refractories, Glass and Enamels at the National Technical University – Khar'kov Polytechnic Institute. The database contains structured information on the chemical-mineral composition and the properties of different forms of ceramic raw materials, which was collected from an experimental study of the materials during a systematic investigation of the raw materials base used by domestic manufacturers of construction ceramic.

It was established from the results of a study of the chemical composition of clayey rocks that 33 clays in the fired state contain Al_2O_3 in amounts from 6.0 to 13.5%,[2] which corresponds to the acidic group, and 15 rocks belong to the semiacidic group of clayey raw material with Al_2O_3 content from 14.2 to 27.8%. Analysis of the material composition of the clays showed that the overwhelming majority comprise polymineral varieties, whose clayey part includes mainly minerals of the kaolinite, illite and montmorillonite groups. Chlorite group minerals are present in smaller quantities in some clay. A particularity of the clayey rocks studied is their high contamination with impurities, whose total content in many cases is much greater than that of the clayey matter. The non-clay part of the rocks is represented by quartz, carbonates, gypsum, iron-containing compounds, minerals in the feldspar group and different accessory minerals (zircon, rutile, tourmaline, hornblende, diopside and so forth). Statistical analysis of the experimental sample has shown that among the substances indicated above free quartz is present in the highest amount, comprising in a complex with kaolinite, montmorillonite and hydromica the mineral base for clays of this type. A graphical illustration of the mineral composition of clays, reduced to the four basic components, is presented in Fig. 1. The tetrahedron obtained is divided into three sectors depending on the quartz content in the clays: < 25%, 25 – 50% and 50%. It follows from Fig. 1 that most of the clays studied are sandy and contain free quartz in amounts 40 – 70%. The real content of free quartz in clay will be somewhat lower (30 – 60%) owing to the remaining impurities (carbonates, feldspars and accessories). The most commonly found content of the latter substances in the clays studied is 10%, which was also found by statistical analysis of an experimental sample.

[2] Here and below, content by weight.

TABLE 1. Post-Enrichment Mineral Composition of Clays

Mineral type of the clay	Content, wt.%		
	Clayey mineral	Quartz	Carbonates, feldspars, accessory minerals*
Kaolinite	70 (kaolinite)	20	10
Hydromica	60 (hydromica)	30	10
Montmorillonite	83 (montmorillonite)	10	7

* The minerals in the list are arranged in order of decreasing amounts in clay.

The three least contaminated montmorillonite clays with different rock-forming minerals (kaolinites, hydromica and montmorillonite) were chosen to solve the problem posed. To increase their content of the clayey material the rocks were enriched elutriation after which the clay suspension was passed through a No. 0056 sieve. The results of a study of the mineral composition of the enriched clays, which was determined by x-ray phase and petrographic methods of analysis, are presented in Table 1.

The simplex-lattice method of planning an experiment (third-order Scheffé plan) with enriched clayey materials, presented in Table 1, participating as variables was used. Model mixtures of enriched clays with 30, 40 and 50% free quartz were prepared. Large quantities of free quartz were not considered because when raw material is oversanded, in practice, additives with low sand content must be introduced, which, in turn, results in a corresponding decrease of the quartz fraction in the mixture. In the event that quartz is deficient a prescribed amount of free quartz in the mixtures was attained by adding quartz sand pre-sieved through a No. 02 sieve. It should be noted that the total content of carbonates, feldspars and accessory minerals did not exceed 10% in any model body, which makes the mineral composition as close as is possible to the real mineralogy of the clayey raw material under study.

Plastic molding of bodies with normal molding moisture content was used to obtain 25 × 25 × 25 mm samples for the experiments. The dried samples were fired in a laboratory muffle furnace at temperatures 950, 1000 and 1050°C with

isothermal soaking for 1 h. The temperature interval chosen corresponds to the working temperature range for the manufacture of masonry and facing brick, ceramic stones, façade tiles and max panels, obtained from coarse-ceramic bodies. For ceramic samples the properties used to check compliance with the standards for such articles (DSTU BV.2.7-61–97) were studied. The water absorption by saturation in water at room temperature (DCTU BV.2.7-42–97), the ultimate compression strength [5], and the structuring factor K_s of the ceramic materials, which indirectly characterizes freeze resistance, were studied [6]. According to this factor the materials with $K_s > 0.85$ are freeze resistant. For the ultimate compression strength of the samples the so-called shape factor δ, which takes account of the dimensions and shape of the laboratory samples and makes it possible to recalculate their strength values for a real article (in the present case δ = 0.8), was used for processing the experimental data.

Mathematical models adequately describing the effect of the mineral composition of the model mixtures on the properties of the ceramic materials were obtained from the experimental results. A graphic interpretation of the results for the water absorption and mechanical strength of the samples is presented in Fig. 2.

As one can see from Fig. 2, an increase in the content of the montmorillonite component in the model mixtures results in lower water absorption of ceramic materials against a background of lower mechanical strength, which is explained by the formation of firing cracks in the samples possibly because of synthesis in the materials of spinel type phases with high proper thermal expansion. An increase in the content of other clayey minerals (kaolinite and hydromica) in the mixtures results in higher water absorption of the materials. In addition, a high content of hydromica adversely affects the mechanical strength of the materials, which is observed for two-component mixtures (kaolinite-hydromica and hydromica-montmorillonite) and three-component mixtures. This effect is strongest in kaolinite-hydromica mixtures.

As the amount of free quartz in the model mixtures increases, the sinterability of the materials decreases, water absorption increases and mechanical strength decreases (see Fig. 2). Thus, for clayey mineral combinations in the region of the diagrams with kaolinite content > 50% an increase in quartz from 30 to 50% results in a two-fold reduction of the ultimate compression strength. Adding free quartz to hydromica and montmorillonite enriched mixtures (> 50% of these minerals) likewise reduces the mechanical strength of the materials but to a lesser extent. The effect of the firing temperature on the properties of ceramic samples in the experimental interval (950 – 1050°C) was not so large, which made it possible not to single it out as an independent factor when constructing diagrams and to study each property only in relation to the mineral composition of mixtures.

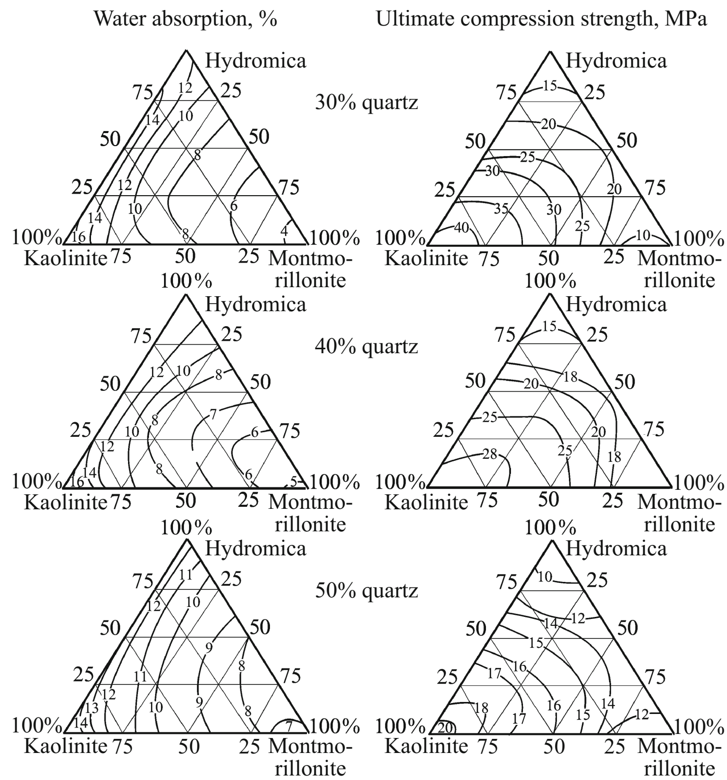

Fig. 2. Effect of the mineral composition of mixtures with 30, 40 and 50 wt.% free quartz on the water absorption and ultimate compression strength of ceramic materials obtained at temperatures 950 – 1050°C.

The information obtained on the effect of the mineral composition of mixtures on the properties of ceramic materials shows that if the montmorillonite component predominates in clay compositions with quartz content from 30 to 40%, the sensitivity to firing of the materials and crack formation increases. Clayey mixtures with higher quartz content (50%) are insensitive to firing. Even though the water absorption of samples obtained from such mixtures (4 – 9%) is the lowest possible, their ultimate compression strength does not exceed 25 MPa even with the minimum content of free quartz. Using mixtures with high content of the hydromica component as a basis, it is possible to obtain materials with average water absorption (8 – 15%) and low ultimate compression strength (the maximum indicator is 23 MPa). Materials obtained from oversanded mixtures enriched with kaolinite and water absorption varying from 8 to 16% depending on the content of free quartz exhibit the highest mechanical strength (maximum indicator 40 MPa).

Generalized diagrams (Fig. 3) were constructed on the basis of the established effect of the mineral composition of oversanded clayey mixtures on the properties of ceramic materials as well as the graphical dependences presented in Fig. 2.

The mineral compositions of clayey raw material that can be used to obtain in the temperature range 950 – 1050°C ceramic materials with the properties of masonry and facing

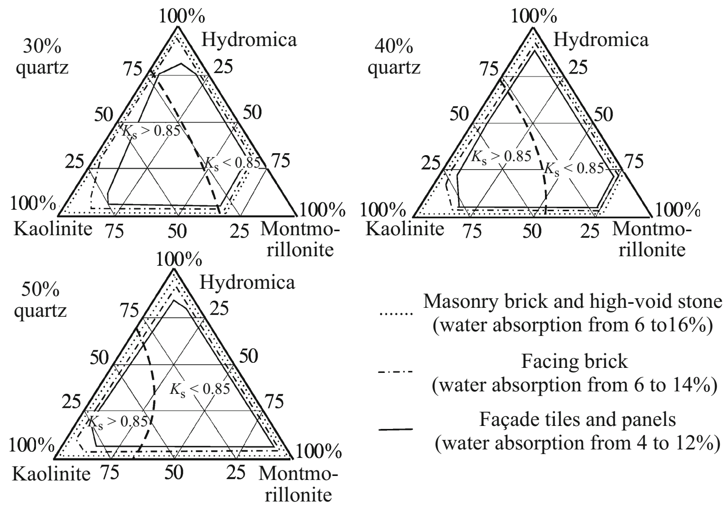

Fig. 3. Mineral composition regions for clayey raw material suitable for the manufacture of wall and façade ceramic in the temperature interval 950 – 1050°C (quartz content 30, 40 and 50 wt.%).

brick, ceramic stone and façade panels meeting the standards for such products are identified in the diagrams. The dotted lines in the diagrams mark mineral compositions that give freeze-resistant ceramic materials ($K_s > 0.85$). It is evident in Fig. 3 that wall and façade ceramics can be produced on the basis of a wide range of combinations of clay-forming minerals. It should be noted that for façade articles the limiting factor is the content of montmorillonite and kaolinite in the clays, and ordinary articles only the content of montmorillonite is limiting. Thus, increasing the amount of montmorillonite in the mixture expands the region where all forms of ceramic material studied are obtained, but at the same time degrades their freeze-resistance and overall quality. Increasing the quartz content in clays from 30 to 50% halves their montmorillonite content admissible for obtaining high-quality freeze-resistant product (from 70 to 35% in the four component mixtures presented).

In summary, the generalized diagrams presented (see Fig. 3) can be used to determine the ratio of the main clay-forming minerals and free quartz in raw materials, which is necessary in order to obtain one or another type of construction ceramic from those studied in the present work. The information obtained using diagrams makes it possible to solve the inverse problem also — to predict the industrial applications of clays from new deposits based on existing data on their mineral composition, which is very helpful for geological exploration specialists and manufacturers of ceramic products. The solution to such a problem reduces to converting the amount of clayey matter in the clays studied to three components (kaolinite, montmorillonite and hydromica) and plotting the points of this composition in one of the generalized diagrams in Fig. 3 depending on the free quartz content in the clay. The suitability of the raw material for obtaining one or another form of ceramic product is determined from the position of this point. In addition, if necessary, the mineral composition of the clayey raw materials can be adjusted on the basis of the diagrams by using clayey additives with a different composition to attain the required material properties. All this creates the basis for a scientific approach to the development of body compositions based on oversanded polymineral clays in order to obtain ceramic construction materials with prescribed properties.

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